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(19)

(72) Inventors:
Geoffrey Arthur Byrne
Ross Ian Aylott

(54) AN ACCUMULATOR FOR ORGANIC MATERIALS

(71) We, INVERESK RESEARCH INTERNATIONAL, a British Company of Inveresk Gate, Musselburgh, Midlothian, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a device for accumulating organic materials from water systems. In particular, the device can be used to monitor the concentrations or variations in concentration of organic pollutants which are potentially toxic or harmful to aquatic and human life and which are derived from effluent discharged into rivers, estuaries and seas, or derived from other sources by removing and analysing samples from said device.

There is worldwide concern over environmental pollution by organic pollutants which may be discharged into rivers, estuaries, seas and inland waterways. Although these compounds may be present in small quantities, it is known that certain types of these compounds accumulate in aquatic plants and fish. Concern has been expressed about many organic compounds, for example, chlorinated materials such as dieldrin, aldrin and benzene hexachloride.

It is desirable to know whether there is an accumulation of such compounds over an extended period of time and to what extent any accumulation can be related to factors such as effluent composition, tidal behaviour, and river flow. It is also desirable to establish a relationship between the accumulated total of a compound collected at any point over a known period of time and the average concentration in water passing that point during that period. An aid to the identification and quantification of organic compounds present in very low concentrations in aqueous streams (information not easily obtained by conventional analysis of 'grab' samples) is also highly desirable.

Accordingly the present invention provides a device for accumulating organic materials from a water system, the device comprising a housing provided with an opening, a porous membrane adapted to act as a selectively permeable aqueous medium — organic medium interface, means for securing said membrane to said housing at said opening to constitute a selectively permeable barrier at said opening, an organic medium as herein defined within said housing filling said housing to a level at which said organic medium wets said membrane and said organic medium being capable of dissolving at least one type of organic molecule diffusing through said membrane from an aqueous medium in contact with the outside of said membrane.

By the term "organic medium" is meant an organic liquid, an oil-in water emulsion, or a hydrophobic gel, each of which may optionally contain one or more complexing agents for the organic materials to be accumulated.

It is preferred for the organic medium (or herein defined) to be an organic liquid. Suitable organic liquids are benzene, xylene, toluene, hydrocarbons such as hexane and chlorinated hydrocarbons such as chloroform and carbon tetrachloride. However, other organic liquids possessing low solubility in water may be used.

With regard to the porous membrane of the device of the present invention, it is preferred that it be composed of a material selected from regenerated cellulose, vinyl chloride homo-

polymers and copolymers, polyvinylidene fluoride, acrylonitrilepolyvinylchloride and polytetrafluoroethylene.

For optimum operation it is preferred that the device should not be adversely affected by changes in, for example, pH temperature, solids content and biological and chemical oxygen demand of the water.

The device is advantageously constructed to withstand variations in underwater currents and able to operate under a range of hydrostatic pressures. In general, the membrane has to be sufficiently robust to withstand knocks from fast moving solid objects in the water. Also, the membrane should preferably not biodegrade during its working life.

The device is generally designed so that the organic materials from the water under test can diffuse through the membrane at sufficiently high rates to allow accumulation of significant quantities of organic materials within a relatively short time. However, the organic medium should desirably not become saturated with dissolved organic compounds during the working life of the device which acts as an organic compound accumulator.

In general the organic liquid medium is chosen so that the concentrations of the accumulated organic compounds are not significantly reduced by back-diffusion through the membrane. Similarly, significant losses of the organic liquid medium from the device should not occur.

The device is capable of selectively accumulating organic compounds of a particular type, i.e. of a particular solubility. It should not be swamped by organic compounds of no interest which may be present in considerably larger quantities than those organic compounds which are of interest. The trapped organic compounds should be readily processable for analysis once removed from the environment under test.

A preferred system comprises an accumulator device having a glass housing provided with an opening fitted with a regenerated cellulose membrane (Cuprophane [Registered Trade Mark], ex J.P. Bemberg; dry thickness – 10μm; pore size – 0.003μm; water wet thickness – 20μm Approx. Pore Area % of total membrane area – 80) and filled with hexane. Hexane is the preferred organic solvent because it readily dissolves compounds of low water solubility, such as dieldrin, aldrin and benzene hexachloride which we are particularly interested in monitoring, it has very low solubility in water (significant losses of solvent from the accumulator do not occur in practice) and it is effective in preventing biodegradation of the cellulose membrane (this effect occurs at the water – membrane – solvent interface; in the absence of hexane (or carbon tetrachloride, toluene, benzene or other solvents) the cellulose membrane is biodegraded in river water.

The laboratory work and the field trials together with the conclusions reached are now discussed.

We refer first to the laboratory tests, and in particular to the experimental conditions. The present invention is also further illustrated in the following description with reference to the accompanying drawings, in which:–

Figure 1 is a diagrammatic elevation of a device of the present invention having a glass container with a vertical membrane;

Figure 2 is an axial section of a glass accumulator device of the present invention;

Figure 3 is a sectional elevation of the device shown in Figure 2, in position on a river bed;

Figure 4 shows the location of the aqueous/organic liquid interface in a pore of a hydrophilic membrane and also a hydrophobic membrane;

Figure 5 is a graph showing the results of the accumulation of 2-bromopropane by carbon tetrachloride;

Figure 6 is a graph showing the accumulation of dieldrin and γ-benzene hexachloride by hexane;

Figure 7 shows gas chromatograms of a hexane sample taken from an accumulator of the present invention and of a 'grab' sample extract of the water in which the accumulator had been immersed;

Figure 8 shows a partly sectioned elevation of a device of the present invention incorporating a stirrer close to the membrane surface thereof;

Figure 9 is a detailed sectional elevation of the housing of the device shown in Figure 8; and

Figure 10 is a side view of the motor and battery of the motor block of the device of Figure 8.

1. Apparatus

The apparatus used for laboratory studies is shown in Figure 1 of the accompanying drawings. Figure 1 is a diagrammatic elevation of a glass container with a vertical membrane.

A polymer membrane 1 in sheet form is located between the ground glass flanges 2 and 3 of two glass reaction vessels 4 and 5 respectively. Each flask is fitted with a side arm 6 and 7 for filling, stirring (when required) and sampling purposes. Although gaskets were used for initial laboratory studies it was later shown that their presence was not essential and that solvent leakage did not occur in their absence. The two flasks are held together by spring clips 8. Although chlorinated hydrocarbons have a slight softening effect on polyethylene at room temperature, no adverse effects were noted with carbon tetrachloride; if necessary PTFE gaskets, which are completely unaffected by chlorinated hydrocarbons, could be used instead. Vessel 4 contained an aqueous

solution of an organic compound under test (e.g. dieldrin) and vessel 5 the organic solution (e.g. hexane).

This system was entirely satisfactory for experiments with Cellophane membranes (The word "Cellophane" is a Registered Trade Mark).

The membrane was desired to have the following properties:

i) *High permeability towards organic molecules*: since transport rate is inversely proportional to membrane thickness, very thin membranes were desirable

ii) *High mechanical strength and flexibility*: a balance was necessary between high strength and low membrane thickness

iii) *Chemical resistance and non-biodegradability*: in particular resistance to organic solvents such as hexane and carbon tetrachloride was needed

iv) *Consistent transport behaviour*: i.e. resistance to fouling.

In principle, any polymeric membrane material demonstrating these properties may be used. The usefulness of membranes which are swollen by the organic solvent will depend upon the degree of swelling and whether prolonged swelling results in slow dissolution or mechanical breakdown of the membrane.

Thus, for example, the so-called Gelman (the word "Gelman" is a Registered trade mark) filters in Table I may be used for those solvents with the code G (e.g. triacetate membrane may be used with an accumulator containing carbon tetrachloride but not with one containing chloroform).

Although hydrophobic membranes such as polypropylene can be made to work, we prefer hydrophilic membranes.

2 *Assembly of glass accumulators for laboratory studies*

The Cuprophane membranes contained about 17% glycerol as plasticiser. Before assembly, the glycerol was removed by soaking the membrane in distilled water for 30 minutes and then replacing the water by two successive portions of distilled water. The wet membrane was then fitted across the face of the accumulator as shown, still in the wet condition. Both compartments of the accumulator were then filled. Any small amount of water remaining on the surface of the 'trapping side' of the membrane became detached during filling and floated to the top of the organic liquid from where it was easily removed with a pipette. This effect occurred very infrequently.

In stirred systems, the stirrer (of the double link glass variety) was located centrally in the relevant compartment.

Temparature control is effected by locating the accumulator in a constant temperature (±0.5°C) water bath.

3 *Assembly of glass accumulators for field trials*

The design of glass accumulators adopted for field work was shown in Figures 2 and 3 of the accompanying drawings.

Figure 2 is an axial section of the accumulator; and Figure 3 is a sectional elevation of the device of Figure 2, in position on a river bed.

The device 9 shown in Figure 2 comprises a glass container 10 filled with an organic solvent 11. The glass container 10 is covered with a membrane 12 which is held in place by means of a ground glass flange 13, two gaskets 14 and a holding ring 15 having chamfered edges which prevent the membrane from splitting. The flange 13, the gaskets 14, the holding ring 15 and the membrane 12 are fixed in position by means of a flange clamp 16. The glass container 10 is provided with an opening 17 for filling and emptying purposes.

Figure 3 shows the device 9 fitted into a concrete block 18 with the aid of a pipe 19 set into the concrete block 18. The device 9 is supported in position by means of foam support 20. The devide 9 and concrete block 18 are covered by a plasics coated wire cage 21 which is held in position on a river bed 22 by means of stakes 23.

The holding ring was 4 mm thick, the polythene gasket was 0.5 mm thick and the membrane area was about 44 cm^2. The volume when full with trapping agent was about 400 to 700 ml.

Experiments showed that, while the concrete blocks remained stationary in slow to medium flowing water, in heavy spate conditions they were sometimes shifted a few yards downstream. To overcome this problem, the accumulators were staked into the river bed using the procedure shown in Figure 3.

The plastic coated wire cages prevented large stones from damaging the membranes. They were particularly useful in collectin leaves and weed, which otherwise would block the membrane surface.

Accumulator Preparation: Installation in and Removal from Test Site

i) *Filling procedures.* Membranes were cut approximately to size and soaked in distilled, deionised water over-night to remove plasticiser. Polythene gaskets were treated similarly.

The accumulators were assembled as follows (see Figure 3)

a) support accumulator in cork ring

b) locate polythene gasket

c) locate membrane ensuring uniform tension

d) locate second polythene gasket

e) locate thick plastic fixing ring (~ 4 mm thick)

f) fasten clamp

g) invert accumulator and fill with organic solvent solution (excessive membrane expression may be prevented by means of a back plate placed against the membrane during

TABLE 1.

CHEMICAL COMPATIBILITY OF GELMAN FILTERS

Chemical	Filter							
	Triacetate Metricel* Type GA, Type P.E.M. Coloured Metricel	Vinyl Metricel*	Fluoride Metricel*, Type VF	Alpha Metricel*	Acropor*, Type AN	Acropor*, Type WR	Epoxy Versapor	Polypropylene
ALCOHOL								
Methanol	F	G	G	G	G	G	G	G
Ethanol	G	G	G	G	G	G	G	G
Isopropanol	G	G	G	G	G	G	G	G
Propanol	G	G	G	G	G	G	G	G
Butanol	G	G	G	G	G	G	G	G
Amyl	G	G	G	G	G	G	G	G
Tetrahydrofurfuryl					P	G		
ESTERS								
Methyl Acetate	D	P	F	G	P	F	G	G
Ethyl Acetate	P	P	F	G	F	F	G	G
Isopropyl Acetate	P	P	G	G	G	G	G	G
Butyl Acetate	P	P	G	G	G	G	G	G
Amyl Acetate	F	G	G	G	G	G	G	G
Cellosolve Acetate	P	P	G	G	G	G	G	G
KETONES								
Acetone	P	P	P	G	P	P	G	G
Methyl Ethyl Ketone	D	P	F	G	P	F	G	G
Methyl Isobutyl Ketone	P	P	G	G	F	G	G	G
Cyclohexanone	D	D	P	G	P	P	G	G

TABLE I CONTINUED

Chemical	Filter							
	Triacetate Metricel Type GA, Type P.E.M. Coloured Metricel	Vinyl Metricel	Fluoride Metricel, Type VF	Alpha Metricel	Acropor, Type AN	Acropor Type WR	Epoxy Versapor	Polypropylene
GLYCOLS								
Ethylene	G	G	G	G	G	G	G	G
Propylene	G	G	G	G	G	G	G	G
Glycerine	G	G	G	G	G	G	G	G
GLYCOL ETHERS								
Methyl Cellosolve*	P	F	G	G	G	G	G	G
Butyl Cellolsove*	F	F	G	G	G	G	G	G
ETHERS (MISC.)								
Diethyl	G	G	G	G	G	G	G	G
Petroleum	G	G	G	G	G	G	G	G
Diisoporopyl Ether					G			G
Tetrahydrofuran	D	D	P	G	P	P	G	G
Dioxane	D	P	P	G	P	P	G	G
HALOGENATED HYDROCARBONS								
Chloroform	D	P	G	G	F	G	G	G
Methylene Chloride	D	D	G	G	P	G	G	G
Carbon Tetrachlor-ide	G	G	G	G	G	G	G	G
Trichlorethylene	G	F	G	G	G	G	G	G

TABLE I CONTINUED

Chemical	Filter							
	Triacetate Metricel Type GA, Type P.E.M. Coloured Metricel	Vinyl Metricel	Fluoride Metricel, Type VF	Alpha Metricel	Acropor, Type AN	Acropor, Type WR	Epoxy Versapor	Polypropylene
HALOGENATED HYDROCARBONS (Contd)								
Freon **TF	G	G	G	G	G	G	G	G
Perchloroethylene	G	G	G	G	G	G	G	G
Chlorothene ***NU	G	F	G	G	G	G	G	G
Gensolv + D					G			G
Dowclene ***WR	G	F	G	G	G	G	G	G
AROMATIC HYDROCARBONS								
Benzene	G	P	G	G	G	G	G	G
Toluene	G	P	G	G	G	G	G	G
Xylene	G	P	G	G	G	G	G	G
Naphthalene	G	P	G	G	G	G	G	G

CODE

G = Good, no effect
F = Fair, swells, softens, slow solvent action.
P = Poor, not recommended. Destroys filter porosity.
D = Dissolves completely.
** = Trade Mark, E.I. DuPont.
*** = Trade Mark, Dow Chemical Co.
+ = Trade Mark, Allied Chemical Co.
* = The words Cellosolve, Metricel and Acropor are Registered Trade Marks.

NOTES

1. The Gelman membranes are made by the Gelman instrument Co. Ann Arbour, Michigan, U.S.A.
2. Triacetate = cellulose triacetate. Vinyl metricel type VM is a polyvinyl chloride. Fluoride metricel, type VF is polyvinylidene fluoride.
Alpha metricel is a regenerated (from rayon) cellulose acropor type and is an acrylonitrile – polyvinylchloride copolymer reinforced with nylon.

filling although with practice this step is not essential).

The whole operation was done as quickly as possible (~ 1–2 min) to minimize the time that the membrane surface was exposed to the atmosphere.

ii) *Location.* The accumulator was then placed, membrane upwards, in a plastic bucket of distilled water and transported to the test site. The accumulators were removed from the buckets and located in the concrete blocks. An alternative method was not to use the plastic buckets but to keep the membrane surface wet by the intermittent application of distilled, deionised water from a laboratory wash bottle. The space between the accumulator and the concrete wall was packed with ½" thick polyurethane foam to provide a firm fit. The plastics coated wire cages were then placed over the concrete blocks and secured with wire ties. The complete assembly was then placed at the chosen site in the river. The site (e.g. river bed) was chosen so that the entire assembly was at least 6 inches below the surface of the water when the water was at its normal lowest level, and the river bed was sufficiently soft to accept holding stakes for the accumulators. The membranes were inclined at about 20° to the flow of water. Modification to the method of fixing was made when the accumulators were placed in a sewage works outfall or in a sewage treatment plant settling tank.

The accumulators were inspected regularly during the trial period. During the trial, the assembly was removed from the water and any leves or other debris were detached from the cage. The cage was removed from the block and the accumulator and membrane rinsed rapidly with distilled, deionised water to remove any dirt or small particles. Normally, the membrane was very clean. Aliquots of the organic solvent were removed for analysis and a known amount of fresh solvent was added to maintain the original volume. At the conclusion of the trial, the whole sample was kept for analysis.

Theoretical considerations

a) *Accumulation process*

Accumulation of organic compounds in the organic solvent occurs only if the organic compound is soluble in the organic solvent. Thus, the extent of accumulation will depend upon the solubility of the organic compound in the organic solvent and will be governed by the partition coefficient. The process of accumulation therefore is one of solvent extraction. The main difference from normal solvent extraction procedures is that the two essentially immiscible solvents are separated by a membrane, which permits organic molecules to pass from the aqueous phase into the organic phase, but which prevents significant transfer into the organic phase and *vice-versa*; Another difference from normal solvent extraction procedures is that whereas agitation of the aqueous phase may occur (either in the laboratory equipment by the gas stirrer (figure 1) or by virture of the flow of water over the membrane in a river or sewage works outfall), the organic phase in the design of accumulator is unstirred.

Movement of water on the membrane surface will minimize boundary layer effects; and rapid movement will increase the rate of transfer of organic compounds across the water-solvent interface.

Lack of agitation in the organic phase will, therefore, minimise the 'back-diffusion' of accumulated organic materials which would occur when an equilibrium situation was disturbed as a result of a decrease in the equilibrium solute concentration in the aqueous phase. Thus in the practical situation, e.g. a flowing river, where the concentration of organic compound in the river may vary during the accumulation period, it is theoretically possible for the accumulator to contain more organic compound than would be forecast from a knowledge of the partition coefficient and the *average* concentration of organic compound in the water during the test period (i.e. a true equilibrium system might never be achieved).

b) *Surface properties of polymer membranes*

In the case of two different membranes, for example one made from Cellophane (regenerated cellulose) and the other from polytetrafluoroethylene, (PTFE), the polymers have different surface properties (surface energies). Cellophane is hydrophilic and therefore more easily wetted by water than by carbon tetrachloride. PTFE is hydrophobic and more easily wetted by carbon tetrachloride than by water. These properties are likely to determine the location of the aqueous-organic liquid inter-face in the proposed accumulator systems which, in turn, may affect the rate of transfer of organic compounds across the membrane. The two systems may be represented as shown in Figure 4 of the accompanying drawings. Thus, for a hydrophobic membrane the aqueous-organic liquid interface is nearer to the aqueous compartment of the accumulator; the opposite is true for the hydrophilic membrane. Consider the transfer of an organic molecule through the pores of the hydrophilic and hydrophobic membranes. Since the rate of stirring of the aqueous phase is ~~unlikely~~ to affect diffusion through stationary liquid in the pores and if it is assumed that the kinetics of transfer across the water-solvent interface are similar in both systems then it can be seen that transfer through a hydrophobic membrane should be faster than through a hydrophilic one; such differences are likely to be slight. However, other properties may determine the choice of membrane, e.g. organic solvent may be lost more easily through a hydrophobic membrane due to the greater proximity of the

water-organic interface to the exterior of the device.

c) *Organic solvent*

The properties of the organic solvent are of major importance. It should exhibit high affinity for the organic molecules under investigation, thereby preventing the accumulator from becoming saturated with accumulated organic molecules during its life-time. Carbon tetrachloride and hexane were preferred for initial studies because of their higher solubility for many organic pollutants of current interest and because of their low solubilities in water. The solubilities of carbon tetrachloride and hexane in water at 20°C are about 0.77 g/l and 0.14 g/l, respectively.

Carbon tetrachloride is more dense (1.59 g/cm^3 at 20°C) and hexane is less dense (0.66 g/cm^3 at 20°C) than water or dilute aqueous solution of organic compounds. However, no major problems were experienced due to the leakage of organic solvent through the membrane as a result of differential pressure at the membrane surface.

It is important that the solubility of the trapped species is high enough to prevent their precipitation during the anticipated life-time of the accumulator.

d) *Biochemical stability of the membrane*

It is necessary that the membrane exhibits good biochemical stability in the test environment. It was observed that membranes (regenerated cellulose) showed distinct evidence of biodegradation when they were immersed *alone* in a river or sewage works outfall for periods of between 3 and 6 weeks. However, none of the accumulator membranes showed evidence of biodegradation after eight weeks' immersion in such test sites. This biochemical stability is probably due to the anti-bacterial action of the organic solvent which occurs at the water-solvent inter-face in the membrane.

EXAMPLES

The following examples demonstrate the potential of the device.

Table II shows data on the accumulation from dilute aqueous solutions of m-xylene, cresol, dichloromethane and 2-bromopropane by carbon tetrachoride and from dilute aqueous solutions of dieldrin by hexane.

Figure 5 shows the results of the experiment with 2-bromopropane graphically; the behaviour is similar to that observed with the other compounds. These data demonstrate the technical feasibility of the device.

Figure 6 shows the results of a field experiment in which an accumulator filled with hexane was circulated slowly in a secondary sedimentation tank of a sewage effluent treatment plant. Aliquots of the hexane were analysed periodically. The amounts of dieldrin and γ-benzene hexachloride in the hexane increased with time. The experiment was stopped after 5 weeks and the membrane was found to be in good condition. Had the experiment been continued the indication was that accumulation of these compounds would have continued assuming, of course, that the compounds (which are essentially non-biodegradable) were still present in the water.

Further evidence of the usefulness of the accumulator was provided by comparing the gas-chromatogram of the hexane in the accumulator with that of a hexane 'grab' sample extract of the water in which the accumulator had been immersed (sewage effluent treatment plant) the chromatograms (Figure 7) were similar.

Evidence of accumulation of other unidentified compounds (though to be halongenated compounds) was provided from this analysis.

After 5 weeks the amounts of dieldrin and γ-benzene hexachloride accumulated were 2.1μg (i.e. 6.0 x 10^{-3} ppm in a 360 ml volume accumulator) and 3.0μg (8.4 x 10^{-3} ppm), respectively. Insufficient 'grab' samples of the water were taken to provide a reliable statistical average concentration of dieldrin and γ-benzene hexachloride in the water over the 5 week period, but typical 'grab' samples gave concentrations of 0.03 to 0.13 μg/l dieldrin and 0.42 to 0.77μg/l γ-benzene hexachloride.

The above data were obtained in a system in which the movement of water across the membrane surface was relatively slow. It is forecast that increased accumulation would have been found if a faster flow across the membrane had occurred.

In another experiment in a fast-flowing outflow from a different sewage treatment plant, 1.5μg dieldrin and 4.7μg γ-benzene hexachloride were accumulated. These materials were not detected in a single 'grab' sample of water.

All the above data were obtained with accumulators fitted with membranes of area approximately 44 cm^2. Greater accumulation could have occurred with membranes of greater area.

The results of this experiments show that the device will operate in the expected manner in a practical situation.

The uses and potential advantages of the device are as follows:

i) It will concentrate pollutants present at or below levels near the limits of reliable detection — and therefore aid pollutant identification and/or provide useful information on pollutant background levels.

ii) The amount of pollutant accumulated may, in some circumstances, be mathematically related to the average pollutant concentration in the aqueous system: and the device should be sensitive to short-term surges in pollutant concentration.

iii) Selective accumulation of soluble organic compounds is possible by varying the solvent or using mixed solvents

TABLE II

LABORATORY ACCUMULATION EXPERIMENTS

Exp. No.	Organic compound	Initial concentration in aqueous phase, ppm	Accumulating solvent	Concentration of accumulated organic compound ppm at sampling time (hours)
1	m-xylene	100(v/v)	carbon tetrachloride	0(0), 20(2), 24(4), 44(7), 70(24), 68(32), 78(97)
2	o-cresol	120(v/v)	carbon tetrachloride	0(0), 12(2), 16(4), 24(7), 76(24), 92(97)
3	dichloromethane	62(v/v)	carbon tetrachloride	0(0), 30(3), 53(5), 60(21)
4	2-bromo-propane	62(v/v)	carbon tetrachloride	0(0), 24(3), 41(5), 56(21), 56(93),
5	dieldrin	0.4(w/v)	hexane	0(0), 0.04(2), 0.06(4), 0.08(6), 0.30(23), 0.38(31), 0.42(48), 0.43(119)
6	dieldrin	0.004w/v)	hexane	0(0), 0.4(2), 0.7(4), 1.05(7), 1.25(23), 1.60(31), 2.05(39), 2.3(111)
7	dieldrin	0.0014(w/v)	hexane	0(0), 0.6(3), 2.6(22), 2.8(24), 2.8(28), 3.6(45), 4.0(48), 7.6(213)

In experiments 1-6, the volumes of hexane and aqueous phase were approximately the same.
In experiments 6 and 7, the concentrations of accumulated dieldrin should be multiplied by 10^{-3}

iv) Analysis of pollutants is simplified. Very large volumes of water do not have to be processed by time-consuming methods. Direct analysis of accumulated pollutants can be carried out thus minimizing loss of volatile or thermally labile compounds, e.g. solution from the accumulator can be transferred directly to a gas chromatograph or high performance liquid chromatograph. Further concentration of accumulated pollutants, especially those of low volatility, can be achieved by evaporating the solvent. Interference from water-soluble inorganic species is obviated.

v) It is a simple, inexpensive and expendable device. It does not require electrical or other fuel power for its operation. Loss in the field through accident or vandalism would not be a major financial consideration. This tegether with the advantages stated in (iv), could allow organisations with limited financial resources and analytical equipment of modest sensitivity to obtain useful information.

In considering the potential of the accumulator other methods of accumulating organic compounds should be considered in particular adsorption onto charcoal and ion exchange resions. Whilst it is not suggested that the IRI accumulator would be a complete substitute for either of these methods it is suggested that it has several advantages compared to 'adsorption' processes which could make it, if used wither alone or in conjunction with other methods, a valuable tool in environmental monitoring.

Problems associated with 'adsorption' systems, some of which are not found with the present invention, include

i) non-selective adsorption (e.g. it is reported that over 100 non-biodegradable pollutants were extracted from a Rhine waterworks carbon filter). This could, of course, be advantageous in some circumstances

ii) preferential adsorption and blocking of adsorption sites by pollutants or compounds of little interest, present in excess

iii) contamination of system and/or blocking of adsorption sites by silt, weed, etc.

iv) Adsorption of non-soluble pollutants (it is usually desirable to distinguish between dissolved and undissolved pullutants)

v) possible biodegradation of adsorbed species (solvents used in the accumulator of the present invention have been shown to be effective bacteriocides in operation)

vi) necessity of extracting adsorbed pollutants from adsorbent (problems with incomplete recovery, use of large volumes of solvent, and loss of volatile and thermally labile materials have been encountered).

The accumulator is applicable to a wide range of organic pollutants which exhibit high solubility in solvents which are sparingly soluble in water. Relevant classes of pollutants include pesticides, herbicides, lipids, chlorinated and brominated aliphatic hydrocarbons, and poorly-biodegradable industrial chemicals (e.g. nitro aromatics, aromatic ethers, tertiary-butyl substituted phenols, phthalic acid esters, lubricating oil additives).

In particular, if used in properly conducted monitoring programmes, the device will

i) overcome many of the problems associated with conventional sampling and analytical procedures, e.g. it is costly and tedious to take the very large numbers of 'grab' samples necessary for statistical purposes and to process large volumes of particle-containing water

ii) provide a better early warning that pollutant levels were rising, or approaching or had reached dangerous levels; or assurance that control methods were satisfactory

iii) more easily identify sites suitable for research investigation; and conversely, identify sites which require little investigation.

Particular applications include

a) identifying and quantifying pollutants in chlorinated drinking water, waste waters from synthetic monomer plastic-manufacturing and industrial chemical plants

b) plotting pollutant contour maps in estuarial waters or effluent outflows; determining the effectiveness of sequential unit process treatments in effluent plant

c) concentrating organic compounds in drinking water for toxicity testing

d) investigating composition of radioactive materials in waste waters.

CONCLUSIONS

Our laboratory experiments have shown that the device can be used to accumulate organic materials from aqueous solution. Our field experiments have shown that the device can be used successfully in practical situations where a knowledge of the type and amounts of organic pollutants is required.

The method and apparatus of the invention are not restricted to the use of a regenerated cellulose membrane and hexane or carbon tetrachloride as the solvent. The material from which the body of the accumulator device is made should not contain organic materials which can be extracted albeit slowly by the organic solvent. A wide range of other solvents with low water solubilities can be used, depending on the organic compounds being investigated, e.g. benzene, toluene, diethyl ether and ethyl acetate. Similarly, other polymeric membranes than those specifically referred to can be used subject to their compatibility with the organic solvent, their ability to allow the required diffusion processes to occur and their resistance to biodegradation.

The accumulator device can be located for example, on a river bed. However the device need not be immersed directly in the river or effluent stream under test. It is convenient

to locate the device in a bath or other container placed, for example, on the river bank, and to pump the water through the bath or container in a regular fashion.

One improvement in the design of the accumulator is to incorporate a stirring device close to the membrane surface. Mechanical stirring in, for example, slow-moving streams minimises the boundary layer effects and increases the rate of diffusion of organic compound across the membranes. Such a device results in a more constant rate of accumulation than may be found in the device results in a more constant rate of accumulation than may be found in the devices described above. A suitable design is shown in Figures 8 and 9 of the accompanying drawings. A metal housing 24 is provided with an interior lining 25 of glass or other inert material. A membrane 26 is secured to the mouth 27 of the housing 24 as shown below in Figure 9. A motor block 28 is supported above the housing 24 by several connecting rods 29. A motor 37 drives a stirrer blade 30 and is energised by a long-life battery 38 (Figure 10). Figure 9 is a more detailed sectional elevation of the housing 24 which is of stainless steel (the glass or like lining 25 is omitted for clarity). The membrane 26 is held between plastic annuli 31 and 32 respectively.

A cap 33 is threadedly engaged at its lower end 34 with corresponding threading 35 on the outside wall of the housing 24. A filling aperture 36 with a closure means not shown is provided in the base of the housing.

Figure 10 is a side view showing the motor 37 and long-life battery 38 forming part of the motor block 28 (cover omitted). The stirrer 30 has a shaft 39 which enters the motor block through a leak-proof seal 40.

A further modification (not shown) to improve the rate of accumulation is to have a means of stirring the organic liquid.

WHAT WE CLAIM IS:–

1. A device for accumulating organic materials from a water system, the device comprising a housing provided with an opening, a porous membrane adapted to act as a selectively permeable aqueous medium-organic medium interface, means for securing said membrane to said housing at said opening to constitute a selectively permeable barrier at said opening, and an organic medium (as herein defined) within said housing filling said housing to a level at which said organic medium wets said membrane, said organic medium being capable of dissolving at least one type of organic molecule diffusing through said membrane from an aqueous medium in contact with the outside of said membrane.

2. A device according to claim 1, wherein said organic medium is selected from benzene, xylene, toluene, hydrocarbons, chlorinated hydrocarbons and other organic liquids possessing low solubility in water.

3. A device according to claim 2, wherein said organic medium is hexane.

4. A device according to claim 2, wherein said organic medium is chloroform or carbon tetrachloride.

5. A device according to claim 1, wherein said porous membrane is composed of a material selected from regenerated cellulose, vinyl chloride homopolymers and copolymers, polyvinylidene fluoride, acrylonitrilepolyvinylchloride and polytetrafluoroethylene.

6. A device according to claim 1, wherein said housing is composed of glass and is filled with hexane, and said membrane is composed of regenerated cellulose wetted by said hexane.

7. An installation for accumulating organic materials from a water system comprising a device according to claim 6, and further comprising a concrete block provided with an opening for receiving said device and allowing water to flow freely over said device means for supporting said device within said concrete block at the mouth of said opening and means for anchoring said concrete block with said device at a chosen location in a water system.

8. A method of monitoring the organic materials content in a water system comprising the steps of allowing water from the water system to contact one side of a porous membrane capable of allowing said organic materials to diffuse therethrough, maintaining in contact with the other side of said porous membrane an organic medium (as herein defined) being capable of dissolving said organic materials and removing at intervals samples of said organic medium containing said organic materials and analysing said samples to determine the accumulation of said organic materials over a predetermined period.

9. A device for accumulating organic materials from a water system substantially as herein described with reference to Figures 1, 2 and 8 of the accompanying drawings.

10. An installation for accumulating organic materials from a water system as claimed in Claim 7 substantially as herein described with reference to Figure 3 of the accompanying drawings.

Elkington and Fife,
Chatered Patent Agents,
High Holborn House,
52–54 High Holborn,
London WC1V 6SH

Agents for the Applicants

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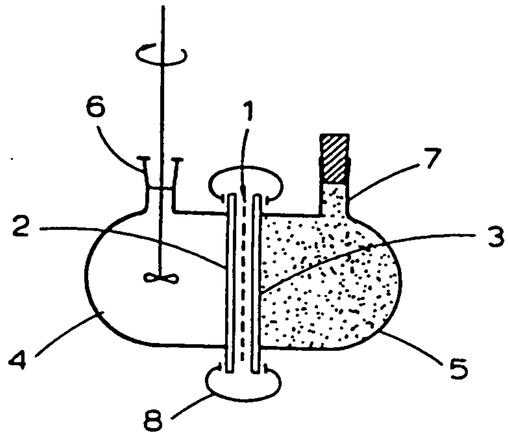

Fig. 1

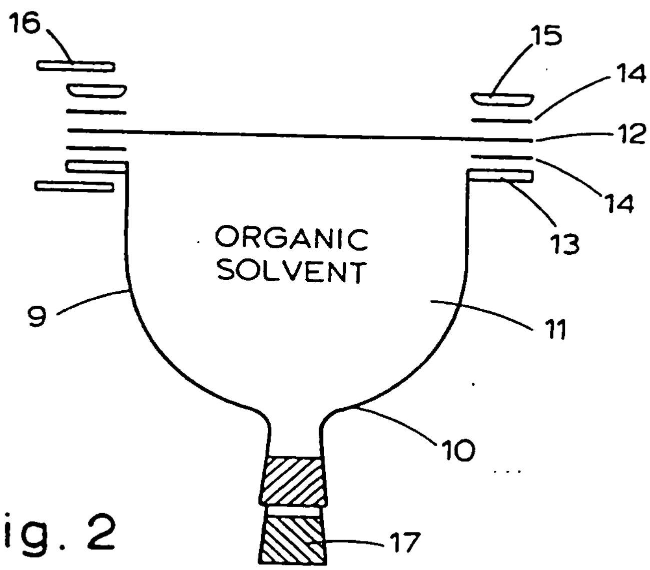

Fig. 2

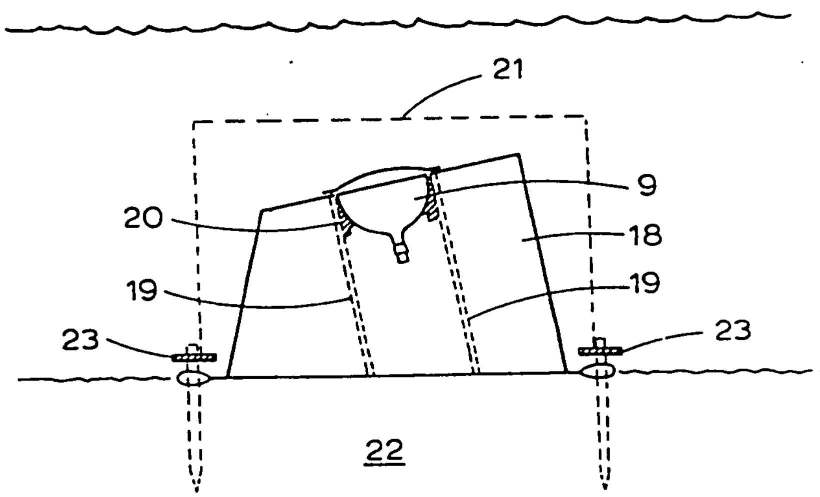

Fig. 3

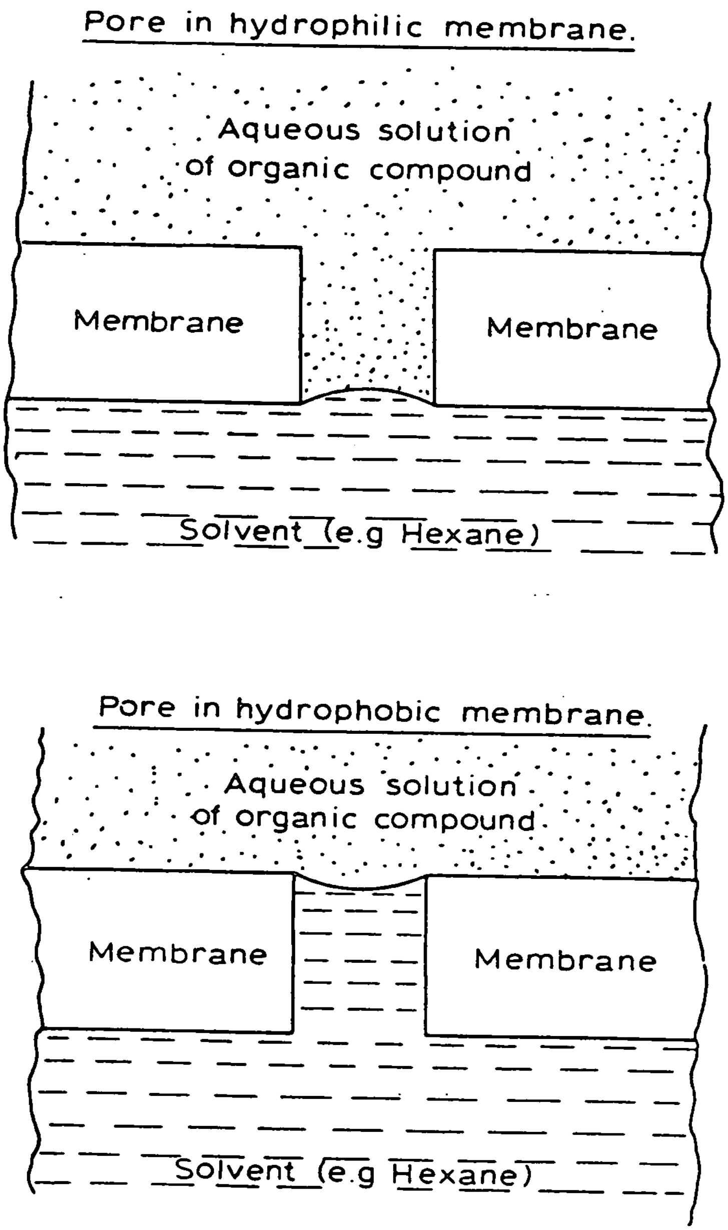
Pore in hydrophilic membrane.
Aqueous solution of organic compound
Membrane
Membrane
Solvent (e.g Hexane)
Pore in hydrophobic membrane.
Aqueous solution of organic compound
Membrane
Membrane
Solvent (e.g Hexane)

Fig. 4

1566253 COMPLETE SPECIFICATION

7 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 4

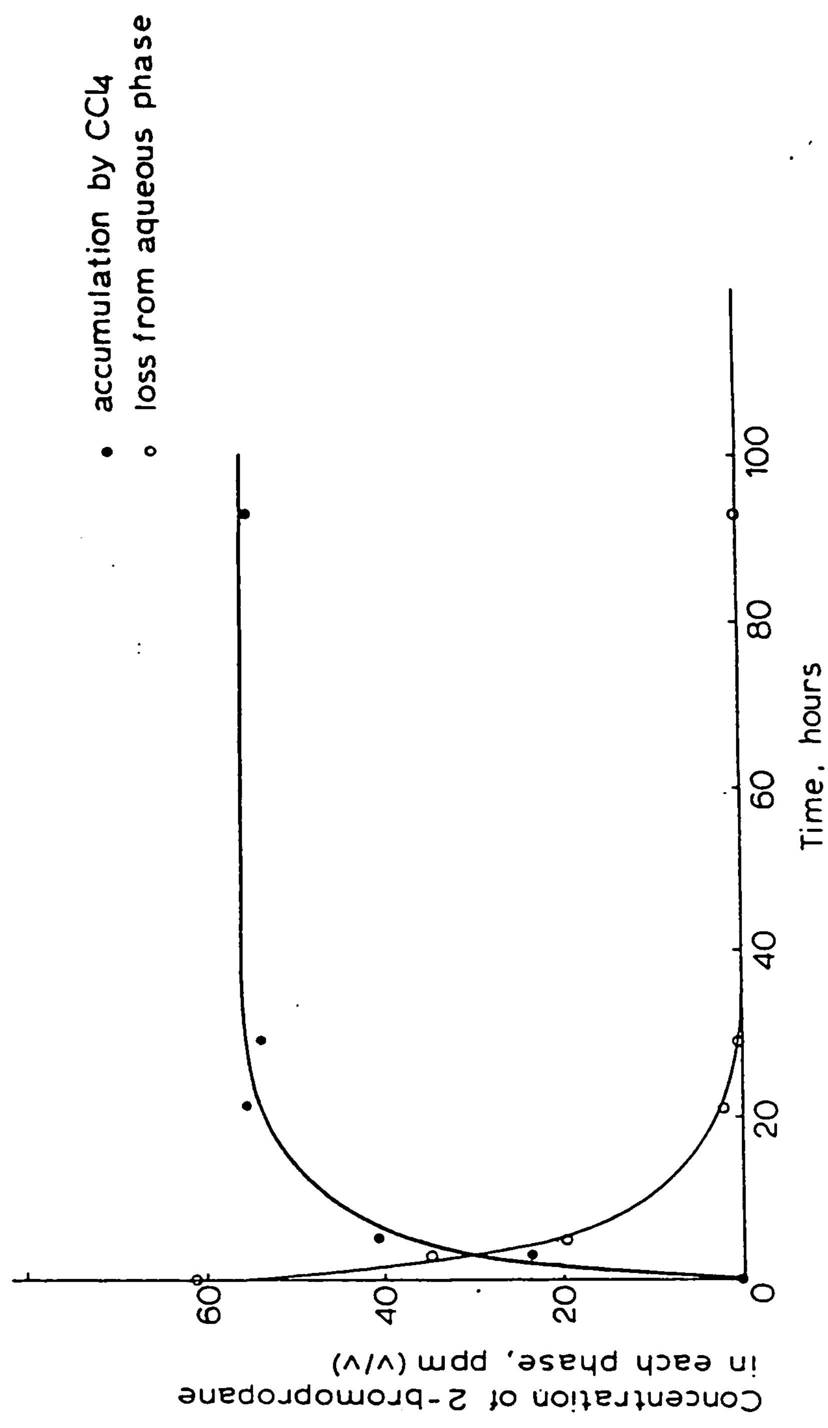

Fig.5

1566253 COMPLETE SPECIFICATION

7 SHEETS This drawing is a reproduction of the Original on a reduced scale

Sheet 5

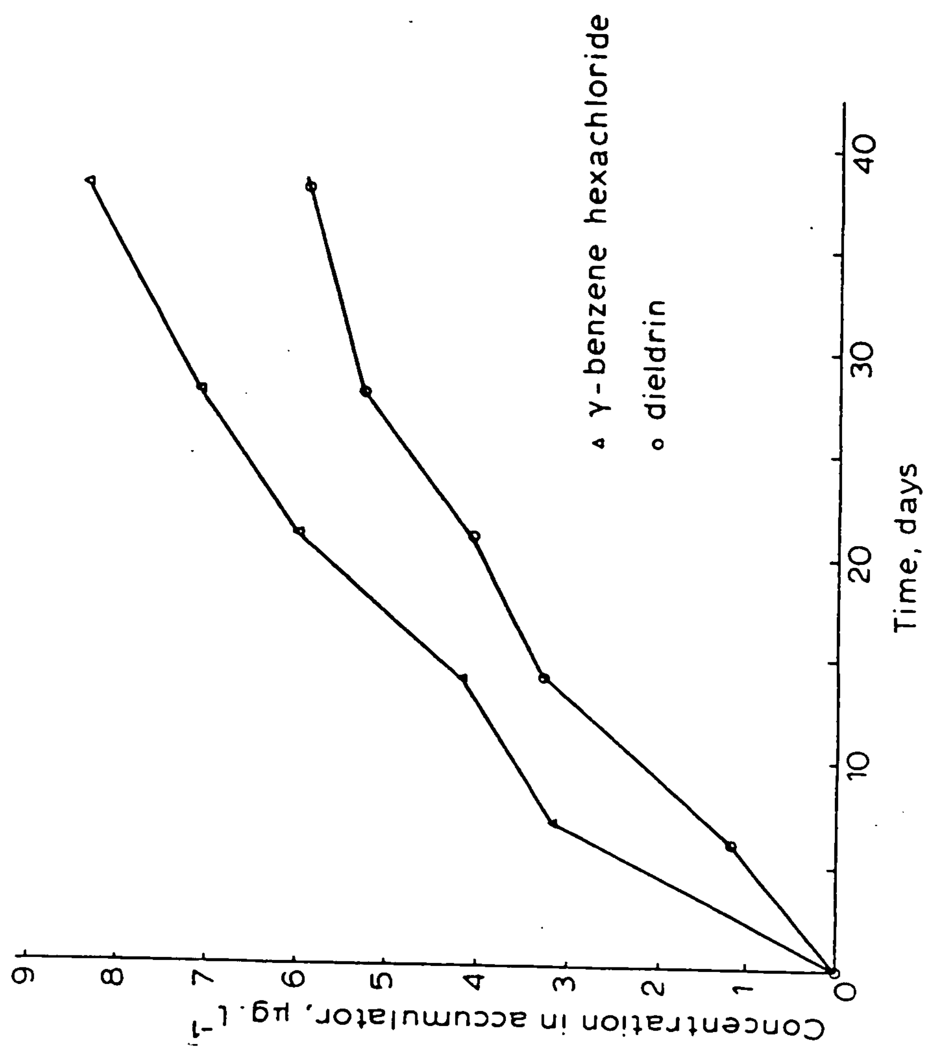

Fig. 6

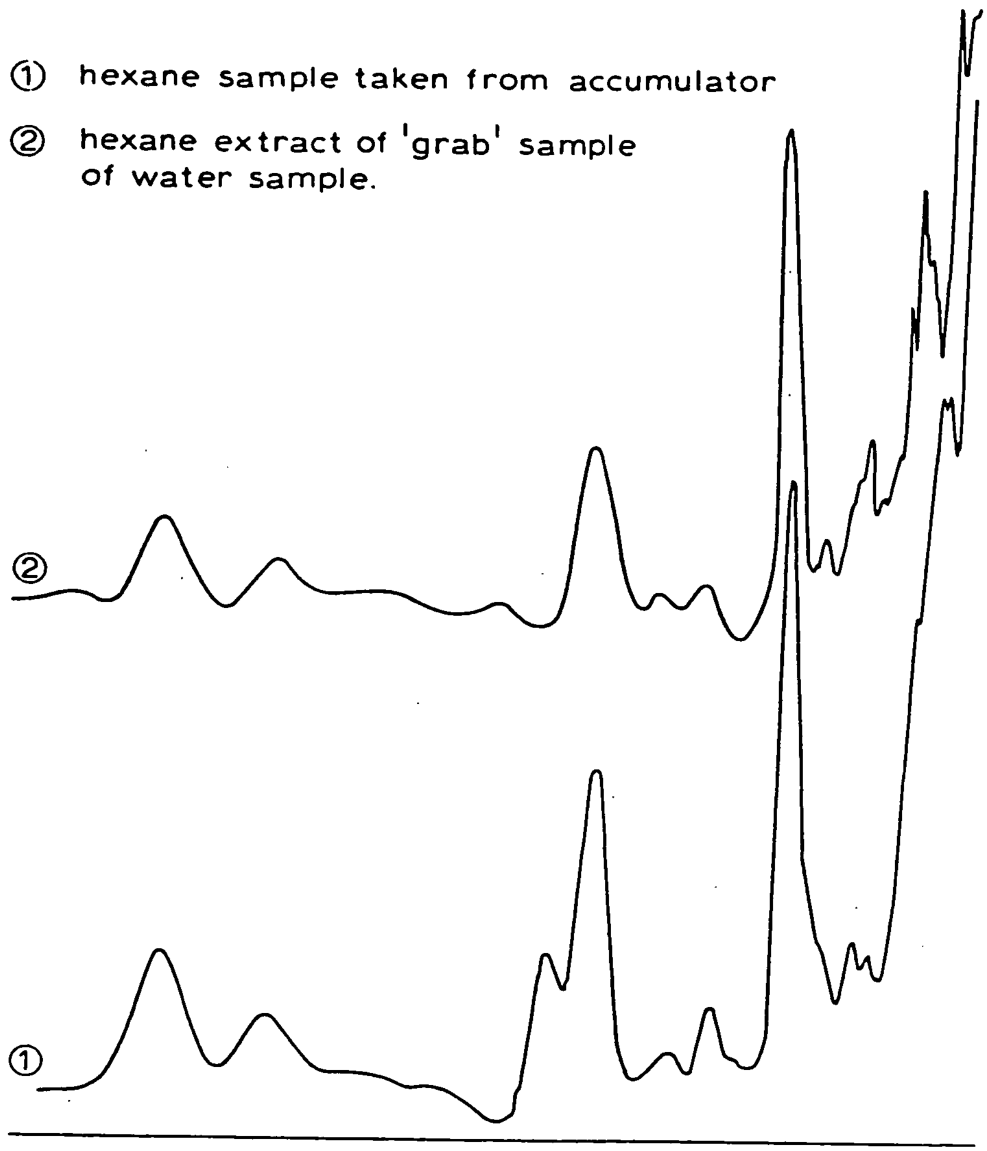
① hexane sample taken from accumulator
② hexane extract of 'grab' sample of water sample.
②
①

Fig. 7

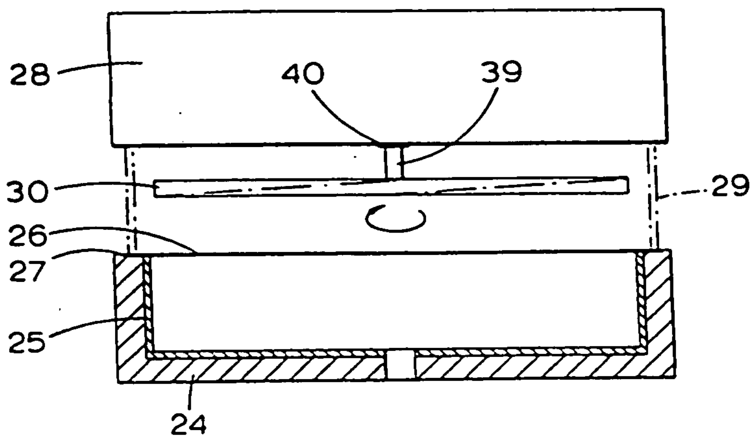

Fig.8

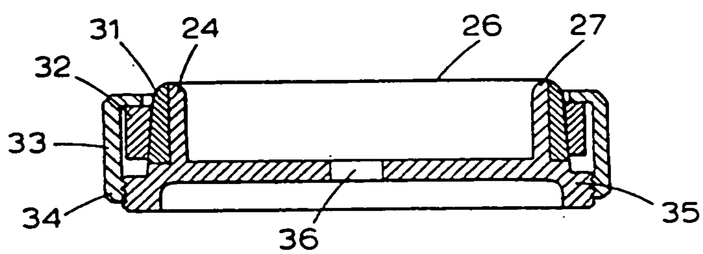

Fig.9

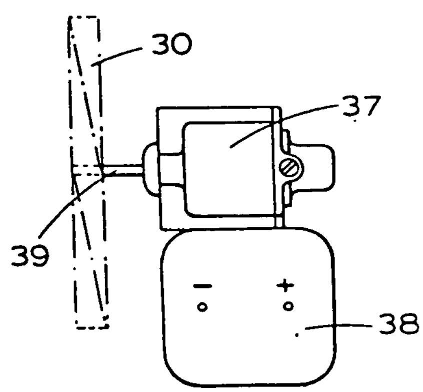

Fig.10

Byrne + Aylott - Patent 1976.